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Estimating the time-varying emission rate of peracetic acid

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Abstract

The use of peracetic acid (PAA) as a general disinfectant has seen increasing usage in recent years, and although it is a strong irritant, exposure monitoring for PAA may often be difficult due to relatively high costs and the potential for interferences by other co-occurring chemicals such as hydrogen peroxide. These issues with exposure monitoring make modeling a potentially useful tool in exposure assessment of PAA if model parameters can be accurately determined. This study estimates the time-varying mass emission rate of PAA for use in exposure modeling by using the small spill model and examines the effect of various environmental conditions on the PAA evaporation rate, including surface roughness/substrate, general ventilation rate, and local wind speed. The relatively high evaporation rate constant (1.18 min^{-1}) determined did not vary significantly with these parameters, suggesting it is applicable across a wide range of common environmental conditions. In addition, in a controlled chamber setting, the first-order decay rate constant for PAA in air was determined to be 0.5 h^{-1}. The corresponding half-life of 83 min is approximately 4 times longer than previous estimates. This decay rate should be accounted for in future modeling and exposure assessments. To evaluate the estimated evaporation rate, trials were conducted in a highly controlled exposure chamber using conditions similar to those found in healthcare settings to compare predicted modeled concentrations to those made by a real-time detection instrument, SafeCide 2.0 (ChemDAQ, Inc.). The results of the trials indicate that the evaporation rate constant and well-mixed room model perform well in predicting the concentration of PAA over a range of conditions. Moreover, the modeling results and measured concentrations across all trials indicate a high potential for overexposure to PAA. Therefore, exposure controls must be adequate when considering the use of PAA as a general disinfectant.

Key words: exposure chamber; exposure modeling; evaporation rate constant; exposure to disinfectant chemicals; mass emission rate; peracetic acid; surface roughness; ventilation rate; wind speed

What's Important About This Paper?

The use of peracetic acid (PAA) as a general disinfectant has seen increasing usage in recent years, and although it is a strong irritant, exposure monitoring for PAA has a number of challenges. This study estimated a time-varying mass emission rate of PAA for use in exposure models that results suggest is applicable across a wide range of common environmental conditions. The use of this rate constant with the well-mixed room model effectively predicts PAA concentrations over a range of conditions and indicates a high potential for overexposure to PAA. Therefore, exposure controls must be used when PAA is used as a general disinfectant.

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Introduction

As one in 31 hospital patients and one in 43 nursing home residents in the United States contract a healthcare-associated infection, at a cost of at least 28.4 billion annually in 2022 (Scott 2009), the need for effective disinfectants and cleaning protocols is well established (CDC 2021). The recent global COVID-19 pandemic has also highlighted the need for proper contamination control through disinfection. PAA has long been used as an industrial disinfectant in food processing, water and wastewater treatment, and the healthcare industry, where it was originally used to clean equipment such as endoscopes. PAA usage as a general disinfectant has increased because it has been marketed as an effective, short contact time (~5 min), no-rinse product with benign breakdown products (Pacenti et al. 2010; Dugheri et al. 2018). When used for general disinfection, PAA is commonly sold in a concentrated product mixture along with hydrogen peroxide, acetic acid, and other stabilizers, and diluted to an as-used concentration of <1% PAA.

Despite increasing usage, relatively few assessments have been completed to assess occupational exposures to workers who directly handle PAA for general cleaning and disinfection (Dugheri et al. 2018; Hawley et al. 2018). PAA is a strong irritant to the eyes, mucous membranes, and respiratory tract, and in 2014, the American Conference of Governmental Industrial Hygienists (ACGIH) established a short-term exposure limit (STEL) of 0.4 ppm (1.24 mg/m^3). A study conducted by researchers at the National Institute of Safety and Health (NIOSH) in 2017 indicated that hospital cleaning staff using a cleaning product containing hydrogen peroxide, acetic acid, and PAA reported work-related eye (44%), upper airway (58%), and lower airway (34%) symptoms, despite concentrations of PAA being measured below the ACGIH STEL (Hawley et al. 2018). Recognizing the potential hazards of PAA, NIOSH proposed but has not yet adopted an Immediately Dangerous to Life or Health value of 0.64 ppm (1.7 mg/m^3) in 2015 (NIOSH 2015), which is relatively close to other PAA exposure limits such as the ACGIH STEL.

Care must be exercised in conducting occupational exposure assessments for PAA, which does not yet have an approved Occupational Safety and Health Administration (OSHA)/NIOSH analytical method, as there is a high potential for interference with hydrogen peroxide. There is a commercially available sampling method using a coated silica gel tube with a prefilter that removes hydrogen peroxide prior to PAA reaction with the tube coating (SKC, Inc., 2023) and the resulting PAA reaction product is then assayed via high-pressure liquid chromatography (HPLC). In addition, a disinfectant product manufacturer published an impinger collection method followed by HPLC analysis (Stastny et al. 2022). A further complicating issue is that the concentration of PAA in a given batch of disinfectant can decrease with time after preparation, resulting in differing PAA exposure levels while performing the same task with exactly the same volume of disinfectant solution at subsequent times after batch preparation. Several manufacturers recommend the use of a prepared (i.e. diluted) batch of PAA-based disinfectant be used within 8 h.

Exposure modeling is a complementary strategy to traditional monitoring in occupational exposure assessments, and previous studies have shown that exposure modeling could provide more accurate exposure estimates when limited monitoring samples are collected (Nicas and Jayjock 2002). Although traditionally underutilized in occupational exposure assessment, modeling of contaminant concentrations has recently increased through their use as a method of achieving compliance with the European REACH regulation (Schlüter et al. 2022) and as a complement to traditional exposure monitoring (Keil et al. 2009, 2023).

Models of varying complexity have been used previously to estimate airborne exposure concentrations from the evaporation of volatile compounds in various settings, including organic solvents in a lab setting, hydrogen peroxide biocides in a healthcare setting, and the use of an acetic acid-based floor cleaner (Nicas 2016; Arnold et al. 2020; Tischer and Roitzsch 2022). An important controlling parameter identified in these modeling efforts has been a chemical's first-order evaporation rate constant denoted as K (min^{-1}). This constant is chemical-specific and previous studies have shown that it may vary based on environmental conditions such as temperature, relative humidity, local windspeed, and evaporation surface type (Gray 1974; Keil and Nicas 2003; Arnold et al. 2020; Keil and Miller 2020). In this study, we establish a method for estimating K for PAA that may be used to model occupational PAA exposures in commonly encountered scenarios.

Methods

Model development

The small spill model (Keil and Nicas 2003; Keil et al. 2009) was chosen for assessing the K constant and thereby, the PAA mass emission rate and room concentration. The small spill model assumes that a fixed mass is initially applied or "spilled" at time 0 and evaporates at an exponentially decreasing rate as the available material diminishes. The disinfection cleaning procedure involves using a wipe cloth applied multiple times to clean a surface in a room, with mass (M) of PAA added by the cloth for each application.

The present study treated each wiping application as a small spill, with an evaporation rate constant of K. In the case of using 1 wipe (i.e. 1 "small spill") for a single application of PAA, the mass emission rate (mg/min) of PAA can be expressed using the small spill model as

$$G_1(t) = MKe^{-Kt}, \quad 0 \le t, \tag{1}$$

where $G_1(t)$ is the PAA mass emission rate due to the first wipe at time t after the application. If additional wipes or applications of PAA follow the first wipe, the number of wiping applications (n), with a time interval (I) between wipes, can be defined as

$$n = \left[\frac{t}{I}\right] + 1, \tag{2}$$

where $[t/I]$ is the floor function of the division of t by I. For the second (n=2, $I \leqq t$), third (n=3, $2I \leqq t$), and nth ($(n-1)I \leqq t$) wipe, each successive emission rate can be expressed as

$$G_2(t) = G_1(t) + MKe^{-K(t-I)}, \quad 0 \le t, \tag{3}$$

$$G_3(t) = G_2(t) + MKe^{-K(t-2I)}, \quad 0 \le t, \tag{4}$$

$$G_n(t) = G_{n-1}(t) + MKe^{-K(t-(n-1)I)}, \quad 0 \le t. \tag{5}$$

In Equations (3) to (5), t is always the time elapsed subsequent to the first application at t = 0. By expanding Equation (5), we obtain

$$\begin{aligned} G_n(t) &= G_{n-1}(t) + MKe^{-K(t-(n-1)I)} \\ &= MKe^{-Kt} + MKe^{-K(t-I)} + \cdots + MKe^{-K(t-(n-1)I)} \\ &= MKe^{-Kt}\left(1 + e^{KI} + e^{2KI} + \cdots + e^{(n-1)KI}\right) \\ &= MKe^{-Kt}\sum_{1}^{n} e^{(n-1)KI} \\ &= MKe^{-Kt}\ \tfrac{1-e^{nKI}}{1-e^{KI}}, \quad t \ge (n-1)I. \end{aligned} \tag{6}$$

To estimate the mass emission rate and K, which are unknown, the well-mixed room (WMR) dispersion model was employed to back-calculate $G_n(t)$ using the measured concentration. The WMR dispersion model is an established construct used to estimate potential occupational exposures from a nonpoint source in a room (Keil et al. 2009; Arnold et al. 2017b). However, in our experiments, we purposely sought to establish a WMR environment through the use of air-moving floor fans. To account for the variation of the emission rate (G) over time, a first-order approximation to the WMR dispersion model has been developed by dividing the study period into small time steps and calculating the concentration based on the previous time step's concentration and the corresponding emission rate (Keil et al. 2009). This method results in a time-varying solution to the WMR dispersion model, which is given as

$$\begin{aligned} C_{\mathrm{model}}(t) = {} & \frac{G_n(t-\Delta t) + C_{\mathrm{in}}Q}{Q + k_{\mathrm{L}}V}\left[1 - \exp\left(-\frac{Q + k_{\mathrm{L}}V}{V}\Delta t\right)\right] \\ & + C(t-\Delta t)\exp\left(-\frac{Q + k_{\mathrm{L}}V}{V}\Delta t\right), \end{aligned} \tag{7}$$

where $C(t)$ is the concentration at time t (mg/m^3); C_{in} is the concentration in incoming air (mg/m^3); Δt is a small time interval; Q is the room general ventilation rate (m^3/min); V is the room volume (m^3); k_{L} is the loss rate due to mechanisms other than ventilation (min^{-1}). This approach of breaking down the model into smaller time intervals can lead to a more accurate representation of the concentration dynamics by effectively capturing the variations in the emission rate. This is particularly important when the emission rate fluctuates rapidly. The time interval (Δt) used in the present study is 0.1 min.

Determination of loss rate due to decay of PAA

The stability of PAA in air has not been well studied. Previous reports have indicated that the decay half-life in air was approximately 22 min, based on a single unpublished industry study from 1997 (Breithaupt 2007; European Centre for Ecotoxicology and Toxicology of Chemicals 2021). This relatively short half-life could have a meaningful effect on the airborne concentration of PAA over a potential exposure period. This first-order decay rate is included as a loss term (k_{L}) in Equation (7). The decay rate of PAA in air was assessed by applying a known mass of PAA via a syringe into a small chamber with a volume of 0.16 m^3 (0.81 m × 0.61 m × 0.33 m) with a small recirculation fan placed inside. The chamber was then sealed so that there was no ventilation (Q = 0 m^3/min) and the concentration of PAA was continuously measured. The decay of PAA in water reported in previous studies indicated a first-order exponential decay function (Pedersen and Lazado 2020), and the data were modeled as

$$C(t) = C_0 e^{-k_{\mathrm{L}}t}, \tag{8}$$

where $C(t)$ is the concentration at time t (mg/m^3); C_0 is the initial concentration at time t=0 (mg/m^3); k_{L} is the loss rate coefficient (min^{-1}); t is the time (min).

This equation is often rearranged as in Equation (9) so that it can be plotted as a straight-line relationship with the slope equal to the decay rate:

$$\ln(C(t)) = \ln(C_0) - k_{\mathrm{L}}t. \tag{9}$$

Experiment setup for estimating evaporation rate (*K*)

To estimate K and the mass emission rate of the PAA from the disinfectant, several scenarios were evaluated in a full-size exposure chamber. The exposure

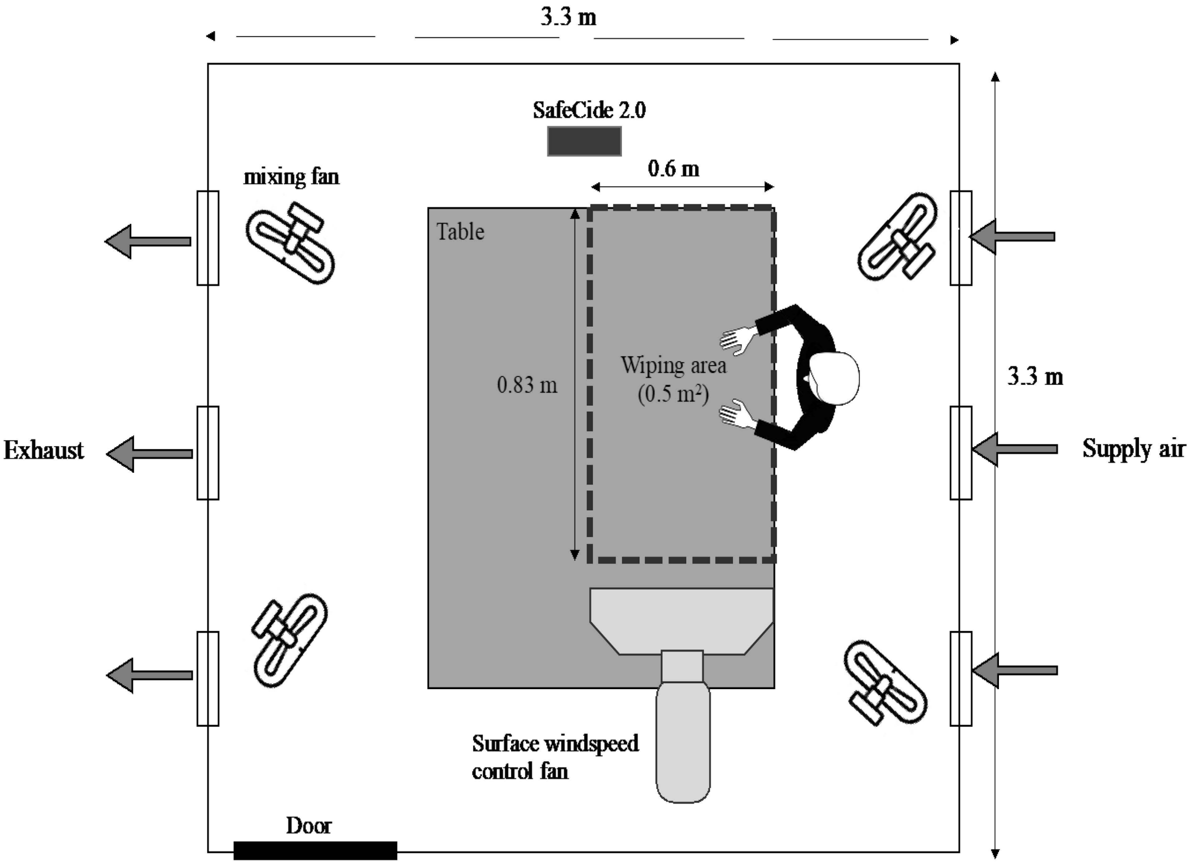

Fig. 1. Chamber diagram (top view).

chamber was constructed of 80/20 framing and aluminum-faced composite panels that do not readily react with a broad range of chemicals (including PAA), with dimensions 3.3 m × 3.3 m × 2.3 m (V=25 m^3). The chamber was exhausted by means of a dedicated exhaust fan capable of maintaining general ventilation airflow (Q) between 0 to ~20 air changes per hour (ACH), as measured by a FastFlo 620S flow meter (Sierra Instruments, Inc., CA, USA). The incoming air into the chamber was preconditioned by the building HVAC (heating, ventilation, and air conditioning) and an upstream conditioning chamber (2.4 m × 3.3 m × 1.5 m; V=12.45 m^3) supplied with a MERV-14 air filter at the inlet. The temperature and relative humidity were ambient within the laboratory and generally held between 68°F and 74°F and 28% and 54%, respectively.

The present study utilized a disinfectant solution consisting of PAA, hydrogen peroxide, and acetic acid for all the tests conducted. This disinfectant is commercially available in a concentrated form containing PAA (5.8%), hydrogen peroxide (27.5%), and acetic acid (5% to 10%), with the balance as water and proprietary stabilizers. This concentrated solution was diluted in the lab at a ratio of 23 ml of concentrate per liter of deionized water to obtain an as-applied concentration of PAA of 0.13%. All diluted disinfection solutions were prepared on a daily basis and were used within 8 h of preparation.

In the experiments for evaluating K, as illustrated in Fig. 1, a table with dimensions of 1.3 × 1.2 m was set in the center of the chamber. To ensure well-mixed conditions, the air was circulated using 4 Lasko 16-inch standing fans located in the corners of the chamber and operated at their lowest settings. The concentration of PAA in the chamber air was measured in real time using a SafeCide 2.0 (ChemDAQ, Inc., PA, USA) portable electrochemical sensor-based gas monitor, which was factory calibrated every 4 months. The PAA sensor module included a proprietary chemical filter that allowed PAA to pass while removing the hydrogen peroxide. The SafeCide 2.0 monitor was positioned at the side of the table, 0.5 m away from both the wall and the table.

Table 1. K estimation testing conditions.

Tests	Ventilation rate (ACH)	Wiping surface	Surface windspeed
K estimation test	2	Lab table	0.06
			0.3
			0.6
			1
	8	Lab table	0.06
		HDPE plastic sheet	
		Metal	
	20	Lab table	0.06
Model validation test	2	HDPE plastic sheet	–
	4		
	8		

During the experiment, a microfiber cloth was soaked in the dilute disinfectant solution for at least 5 min and then wrung out and weighed. The cloth was then used to wipe a 0.5 m^2 area on the table. At the end of 30 s of wiping, the microfiber cloth was weighed again, and then the cloth and container were removed from the chamber. The concentration of PAA was measured until it returned to the background concentration.

To investigate the influence of various environmental variables on the value of *K*, the present study conducted experiments under different environmental conditions, including (a) ventilation rates, (b) surface type/substrate being wiped, and (c) local surface wind speeds. The details of the tested conditions are shown in Table 1, with each condition tested in at least 3 repeated trials. To study the effect of surface windspeed, 4 wind speeds were tested: 0.06, 0.3, 0.6, and 1 m/s, with the general ventilation flow rate set at 2 ACH in the exposure chamber and wiping on a lab table (made of epoxy resin). The surface windspeed was controlled using a directional fan (ECMF-100, TerraBloom, CA, USA) with a hood and was measured using an anemometer (Velometer AVM410, TSI Inc., MN, USA). To study the effect of ventilation rate, the experiments were conducted for ACH values of 2, 8, and 20, with a target surface windspeed of 0.06 m/s and the wiping surface as the epoxy resin lab table. The influence of different surface types was investigated using 3 surface substrates: a lab table (made of epoxy resin), an HDPE (high density polyethylene) plastic sheet, and metal (stainless steel with paint coating) at a ventilation rate of 8 ACH and a target surface windspeed of 0.06 m/s.

To estimate the evaporation rate constant *K*, the experimental design was for a single application (n=1) of mass (i.e. small spill), so the general form of Equation (6) reduces to the traditional small spill model (Equation (1)), which was used to predict the concentration in the WMR model. The emission rate was determined by the least squares method, minimizing the sum of squared difference (ε) between the measured and the modeled concentration. This process involved adjusting the value of *K* and calculating the corresponding mass emission rate and concentrations until the best fit between the modeled and measured concentrations was achieved.

The sum of the squared difference (ε) can be represented by the following equation:

$$\varepsilon = \sum_{t=0}^{T} \left[C_M(t) - C_P(t)\right]^2, \tag{10}$$

where $C_M(t)$ is the measured concentration at time t, $C_P(t)$ is the predicted model (Equation 7) concentration at time t, and T is the total time period of the experiment.

Model evaluation

To test the applicability of the estimated evaporation rate constant *K*, a set of simulated wiping scenarios were conducted to assess the predictive accuracy of the WMR model, incorporating *K*. Modeled concentrations were compared with measured concentrations in defined test chamber scenarios. Six microfiber cloths were soaked in the dilute disinfectant solution for at least 5 min. Then one microfiber cloth was removed from the container, wrung out so as not to be dripping, and used to wipe a 0.24 m^2 section of the HDPE plastic sheet for 2.5 min, at which time the wipe was left on that section of the plastic. This process was then repeated using 6 total wipes for a total time of 15 min. This wiping scenario was consistent with disinfecting an examination room with a volume of 25 m^3 and was based on a standard operating procedure in terms of the type of wipes used and the wet contact time for wipe cleaning with a PAA-based disinfection product in a healthcare setting.

The same wiping procedure was repeated with 3 replicate trials for ventilation conditions within the chamber representing 2, 4, and 8 ACH. The air within the chamber was mixed using 4 Lasko 16-inch floor fans and an overhead-mounted oscillating fan, all operated at their lowest setting, to ensure a well-mixed condition. As the previous experimental trials did not indicate a significantly different value for the evaporation rate constant, *K*, the local windspeed and wiping surface were not varied for the evaluation experiments.

The modeled concentrations for comparison were calculated using the WMR model (Equation 7). Probabilistic modeling was performed by incorporating the distributions of measured and estimated parameters in a Monte Carlo simulation of 1,000 iterations. The general ventilation airflow (*Q*) in the chamber was measured at 5 instances during each trial and modeled as a normal distribution based on the mean and standard deviation of the measurements. The evaporation rate constant *K* was specified as a normal distribution with mean and standard deviation as determined from the replicate trials across all environmental conditions tested in the evaporation rate determination trials. The loss rate coefficient k_L was specified as a normal distribution based on the mean and standard deviation of the replicate trials conducted to test for the decay rate in air. The mass applied per wiping interval was also allowed to vary as this greatly affected the emission rate (Equation 6) and was specified as a normal distribution based on the mean and standard deviation of the weight of the cloths used pre- and post-wiping across all trials. The chamber volume (*V*) and timestep interval (Δt) were set as constants. The mean and 95% confidence intervals of the time-series concentration of PAA within the exposure chamber were calculated using the Monte Carlo simulations and compared with the observed concentrations as measured by SafeCide 2.0. All calculations were performed using R software version 4.1.1 (R Foundation for Statistical Computing, Vienna, Austria).

The performance of the evaluation trials and *K* estimation trials were quantitatively assessed based on performance criteria specified in the ASTM D-5153-97, *Standard guide for statistical evaluation of indoor air quality models* (ASTM International 2019). The set of metrics includes the correlation coefficient (*R*), regression slope factor, normalized mean square error (NMSE), and fractional bias (FB). The correlation coefficient and slope were determined by the linear least square regression with the intercept set at 0. The NMSE and FB can be expressed as

$$\mathrm{NMSE} = \frac{\left(\overline{C_P(T) - C_M(T)}\right)^2}{\overline{C_M(T)}\;\overline{C_P(T)}}, \qquad (11)$$

$$\mathrm{FB} = 2\left(\frac{\overline{C_M(T)} - \overline{C_P(T)}}{\overline{C_M(T)} + \overline{C_P(T)}}\right), \qquad (12)$$

where

$$\overline{C_M(T)} = \sum_{t=1}^{T} \frac{C_M(t)}{T}, \qquad (13)$$

$$\overline{C_P(T)} = \sum_{t=1}^{T} \frac{C_P(t)}{T}, \qquad (14)$$

$$\left(\overline{C_P(T) - C_M(T)}\right)^2 = \sum_{t=1}^{T} \frac{\left(C_P(t) - C_M(t)\right)^2}{T}. \qquad (15)$$

T is the total time period of the experiment.

Results

Loss rate due to decay

The decay rate constant in air was consistent as determined over 12 experimental runs, with a mean of 0.5 ± 0.07 h^{-1}. The linear regression of the log-transformed concentration offset by the initial concentration showed a near-perfect correlation (r^2=0.998) with the first-order rate equation. A decay rate constant of 0.5 h^{-1} translates to a half-life of 83 min, almost 4 times greater than the previously reported 22 min. This PAA loss rate should be accounted for in future exposure modeling.

Evaporation rate under different environmental conditions

The evaporation rates were determined under various conditions. The best estimates of *K* were determined using an optimized applied mass of PAA by minimizing the squared error between the modeled concentration from the small spill model and the measured concentration. Figure 2 illustrates an example of the least square estimation result, showing a close fit between the model curve and the measured data. The results of each *K* estimation test are provided in Fig. S1.

The mass of applied PAA used in the estimates of *K* was allowed to vary across the replicate trials, ranging between 3.84 and 10.0 mg and with a mean (SD) of 6.96 ± 1.64 mg, in order to optimize the model fit through minimizing ε. These estimates of the applied mass of PAA were compared with other independent estimates of the applied mass made using differing methods, including the difference in the weight of each wipe before and after wiping (4.16 ± 0.99 mg), and by averaging the real-time concentration curve from the SafeCide2.0 monitor and multiplying times the ventilation airflow (*Q*), accounting for the decay rate in air (3.41 ± 1.47 mg). Although these 3 estimates of the

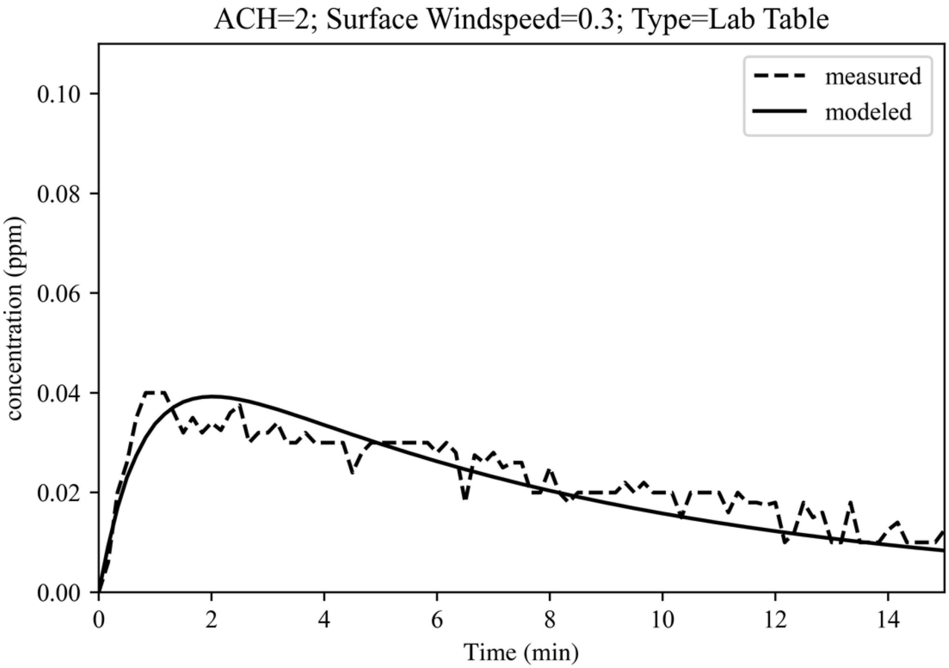

Fig. 2. Minimization result of modeled concentration and measured concentration with surface windspeed 0.3 m s^{-1}, ACH = 2, and wiping on lab table.

applied mass differ, the estimated confidence intervals showed considerable overlap, and the optimized mass value was ultimately used as the best estimate, considering assumptions necessary in the other methods such as the difference in weight of each cloth represented the change in mass of disinfectant solution applied rather than a direct measure of PAA applied and the estimate from the concentration curve assumes perfect mixing in the chamber.

Table 2 shows the metrics of the model performance with all the correlation coefficient and slope factors for the experiments very close to 1, indicating a strong correlation between modeled and measured concentrations. The NMSE for these experiments varies, with values ranging from 0.01 to 0.22, indicating an extremely close match between modeled and measured data. The FB values range from −0.05 to 0.10. All the metrics in the *K* estimation trials met the ASTM criteria (NMSE<0.25, FB<0.25), indicating good precision and accuracy for the least squares estimation.

Figure 3 shows the results of the estimated *K* values. In Fig. 3a, the mean (SD) values of *K* were 1.17 (0.23), 1.21 (0.06), 1.05 (0.25), and 1.19 (0.40) min^{-1} for wind speeds of 0.06, 0.3, 0.6, and 1 m s^{-1}, respectively. In Fig. 3b, the mean (SD) values of *K* were 1.16 (0.18), 1.09 (0.43), and 1.35 (0.37) min^{-1} wiping on the lab table, plastic, and metal surfaces, respectively. In Fig. 3c, the mean (SD) values of *K* were 1.17 (0.23), 1.16 (0.18), and 1.36 (0.07) min^{-1} for different airflow rates of ACH 2, 8, and 20, respectively. The wind speed, ACH, and type of surface did not cause any significant variation in *K* values according to an ANOVA test (*P*-value = 0.73, 0.58, and 0.50 for the different wind speeds, type of surface, and ACH, respectively). Between these 3 groups, i.e. wind speeds, type of surface, and ACH group, *K* had no significant difference either (*P* = 0.85).

These results indicate that PAA's evaporation rate constant does not significantly vary across different test conditions, suggesting that the estimated evaporation rate of PAA can be reliably used in a range of commonly encountered settings. Therefore, all the estimated *K* values were combined for further evaluation, resulting in a mean value of 1.18 min^{-1} and a standard deviation of 0.32 min^{-1}.

Model evaluation

A disinfection wiping procedure was simulated in the exposure chamber based on a standard operating procedure and was modeled using the time-varying emission rate approach described in Equation (6). The PAA mass emission rate as modeled for each wipe, based on the mean parameter values, began at an initial rate of 24.5 mg/min and decreased to 1.4 mg/min at the end of each 2.5-min wiping period as the available mass of PAA evaporated. The time-series concentration is plotted as shown in Fig. 4, with peak concentrations

Table 2. Metrics of the model performance for *K* estimation experiments.

Tests	Ventilation rate (ACH)	Wiping surface	Surface windspeed	Emission rate coefficient (*K*)	ε ($\times 10^3$)	Slope factor	R^2	NMSE	Frac. bias
K estimation test	2	Lab table (synthetic resin)	0.06	0.89	0.46	1.00	1.00	0.03	0.00
				1.46	0.49	1.00	1.00	0.04	0.00
				1.17	0.53	1.00	1.00	0.04	0.00
			0.3	1.27	1.55	1.00	0.97	0.22	−0.05
				1.14	1.81	1.00	0.99	0.13	−0.01
				1.24	2.51	1.00	0.99	0.11	−0.02
			0.6	0.69	2.92	1.00	0.98	0.14	−0.03
				1.21	1.60	1.00	0.99	0.11	−0.01
				1.24	1.15	1.00	1.00	0.04	0.00
			1	1.68	1.28	1.00	1.00	0.04	0.00
				0.69	4.47	1.00	0.98	0.13	−0.04
				1.22	0.89	1.00	0.99	0.02	0.01
	8	Lab table (synthetic resin)	0.06	1.11	0.39	1.00	1.00	0.01	0.02
				1.41	5.37	1.00	0.97	0.07	−0.04
				0.97	3.42	1.00	0.98	0.06	−0.01
		HDPE plastic sheet		0.66	1.61	1.00	0.99	0.03	0.04
				1.68	1.46	1.00	0.98	0.03	−0.05
				0.93	1.59	1.00	0.99	0.03	−0.01
		Paint-coated stainless steel		0.89	2.12	1.00	0.97	0.06	−0.02
				1.39	1.06	1.00	0.99	0.02	0.02
				1.78	0.47	1.00	1.00	0.02	−0.01
	20	Lab table (synthetic resin)	0.06	1.27	0.61	1.00	0.96	0.02	0.06
				1.39	0.52	1.00	0.98	0.02	0.06
				1.43	0.49	1.00	0.96	0.04	0.10

at the end of the 15-min wiping periods of 1.12 ppm and the 15-min time-weighted average (TWA) concentration of 0.72 ppm for 2 ACH, peak concentration of 0.86 ppm and the 15-min TWA of 0.58 ppm for 4 ACH, and peak concentration of 0.54 ppm and the 15-min TWA of 0.41 ppm for 8 ACH. These values all exceeded the ACGIH STEL of 0.4 ppm (as a 15-min TWA) and remained above 0.4 ppm for 33 min (at 2 ACH), 25 min (at 4 ACH), and 8 min (at 8 ACH) (Supplemental Fig. S2). Overall, the model performed well in the context of the ASTM criteria, as shown in Table 3, and as also evident in the time-series plots shown in Fig. 4.

In a few instances (trial 2.1 at 2 ACH, and trials 8.1 and 8.3 at 8 ACH), the measured maximum concentration at the end of the 15-min period was greater than the upper 95th percentile concentration calculated from the Monte Carlo simulations. Similarly, the slope factor in the 8 ACH trials did not meet the ASTM criteria (<0.75) indicating that the model likely underestimated the mass emission rate of PAA in these trials. The emission rate was closely related to the estimates of the applied mass which was subject to the least control in these settings as it depends on the mass of liquid disinfectant on the wipe and the amount of liquid, and ultimately PAA, transferred to the surface. The FB, a measure of systematic bias in the mean concentrations, was also outside of the criteria for 1 trial (trial 2.3 at 2 ACH).

Discussion

Models are useful in assessing exposures for workers (Arnold et al. 2017b), particularly when few monitoring data are available. However, to be effective, key model parameters need to be estimated for a given exposure scenario. The mass emission rate is often the most difficult parameter to estimate since there is typically no straightforward method to measure it. By estimating the emission rate of PAA from the application of the time-varying small spill model based on the evaporation of the contaminant, reasonably accurate estimates of the concentration of PAA in a highly controlled exposure chamber were predicted.

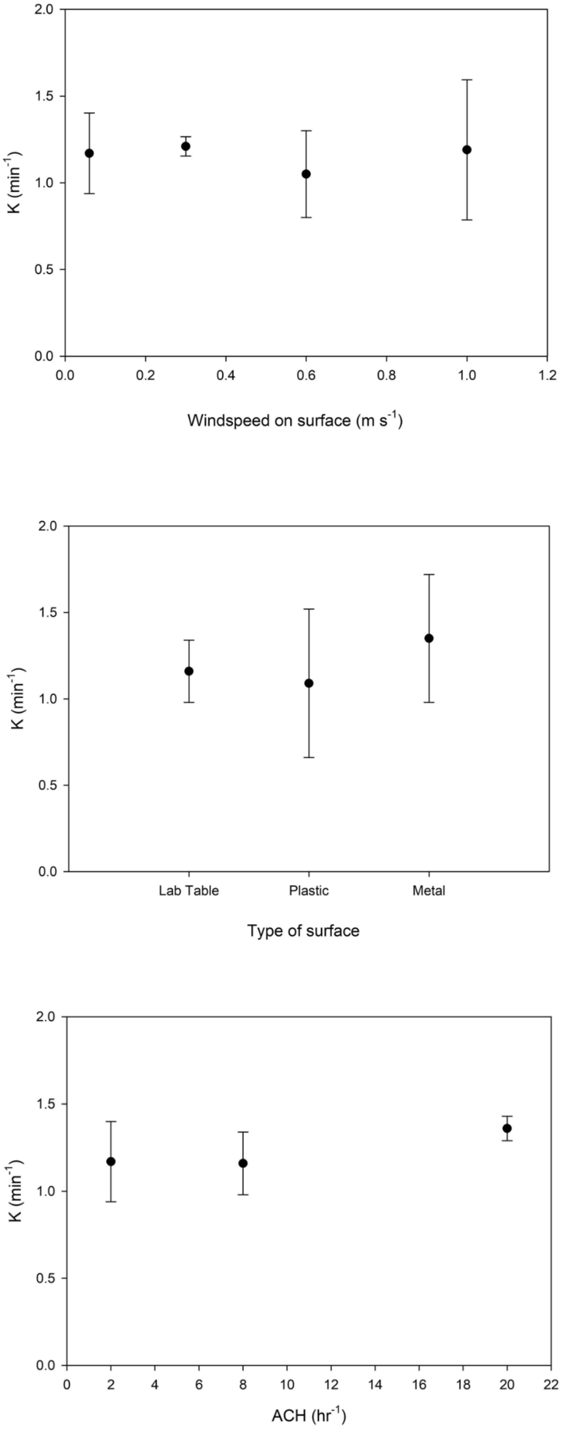

Fig. 3. PAA disinfectant evaporation rate (*K*) with different a) windspeed on the surface (ACH=2, wiping on lab table); b) ACH (windspeed on the surface=0.06 m s^{-1}, wiping on lab table); c) type of surface (ACH=8, windspeed on the surface=0.06 m s^{-1}).

Previous research has related environmental factors to the observed evaporation rate constant K for a volatile substance, including ventilation airflow (Arnold et al. 2020), local windspeed (Gray 1974; Hummel et al. 1996), and surface type/roughness (Keil and Miller 2020). However, in the present study, the K values calculated for PAA were not significantly affected by these environmental conditions. This consistent value for K across the experimental conditions studied, which are representative of traditional occupational settings in healthcare, makes it useful for modeling expected PAA concentrations in general room air.

The results of the evaluation simulations showed good performance relative to the metrics specified in the ASTM standard (ASTM International 2019), including the correlation coefficient of modeled compared with observed concentrations, regression slope factor, NMSE, and FB. In a few instances, the regression slope factor and FB did not meet the accepted ASTM criteria. This deviation from the standard likely reflects the bias observed in the shape of the modeled concentration curves, where modeled concentrations exhibited a curved shape (Supplemental Fig. S2) for each wipe period, representing the rise and fall of concentrations as the emission rate decays over the timestep. The observed concentrations exhibited a monotonically increasing concentration that is believed to be the result of the simulation design where the wipes were left on the table at the end of the timestep and for 5 min beyond the end of the active 15-min wiping period, acting as a continuing source that would not necessarily decay in the same manner as that considered by an applied mass model. Leaving the wipes on the table open to room air following each wipe period served to increase the room PAA concentration. However, used wipes may be left open to room air on a cleaning cart or in an open or unsealed receptacle following their use in hospital settings.

In evaluating the model results in judging the acceptability of the potential exposure relative to the ACGIH STEL, the model performed well in all cases. The leading industry standard in the United States, the American Industrial Hygiene Association (AIHA) *Strategy for assessing and managing occupational exposures,* recommends the use of Exposure Control Categories (ECC) for assessing and managing the risk of occupational exposures (Bullock et al. 2015). In this AIHA framework, the ECC is selected based on a decision statistic of the 95th percentile of the exposure distribution compared with the occupational exposure limit, as opposed to a direct comparison of each measured value. PAA does not have an established regulatory occupational exposure limit but using the ACGIH STEL (0.4 ppm as a 15-min TWA) for comparison,

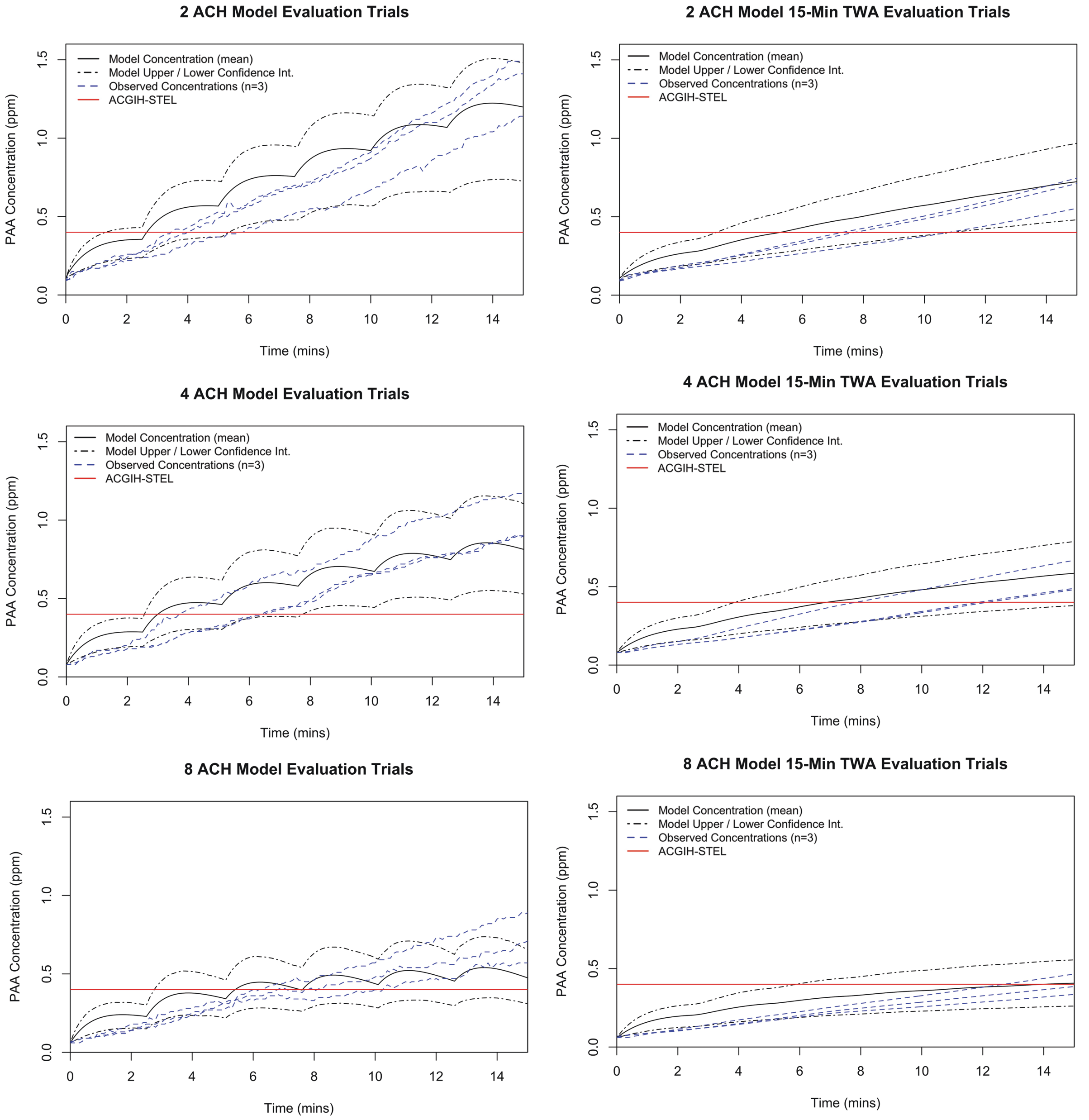

Fig. 4. Results of evaluation experiments compared with modeled concentrations of PAA. Experimental setups consisted of 3 replicate trials of wiping on the HDPE plastic using 6 wipes for 2.5 min each over a 15-min period. a) 2 ACH real-time concentration for active wiping period; b) 2 ACH 15-min TWA concentration for active wiping period; c) 4 ACH real-time concentrations for active wiping period; d) 4 ACH 15-min TWA concentration for active wiping period; e) 8 ACH real-time concentrations for active wiping period; f) 8 ACH 15-min TWA concentration for active wiping period.

both the observed concentrations and the 95th percentile of the model results from the Monte Carlo simulations (as well as the mean of the model results from the Monte Carlo simulations) exceeded the STEL in all 9 trials, indicating an unacceptable Category 4 exposure under the AIHA framework.

Moreover, general room concentrations were predicted by the WMR model, and it would be expected that breathing zone concentrations for a worker's hand wiping PAA would be higher. For example, using a decoupled 2-zone modeling approach (Nicas 2024) in a typical patient room of 50 m^3 with general

Table 3. Results of validation trials showing measured and modeled concentrations of PAA in the chamber over replicate trials (*n*=3) at each given airflow value (*Q*). Probabilistic modeling was performed to model the mean and 95th percentile concentrations, allowing the input parameters to vary in a Monte Carlo analysis with 1,000 iterations. (*Italics indicate outside of ASTM D5157 performance criteria.*)

Airflow (*Q*)	Modeled maximum concentration (ppm) [95 CI]	Measured maximum concentration (ppm)	Correlation coefficient, *R*	Slope factor	NMSE	Fractional bias
2 ACH	1.20 [0.73 to 1.48]	1.49	0.98	0.76	0.04	0.05
		1.41	0.98	0.81	0.03	0.09
		1.14	0.97	1.03	0.20	*0.34*
4 ACH	0.81 [0.55, 1.16]	1.17	0.98	*0.61*	0.06	0.13
		0.90	0.96	0.79	0.07	0.20
		0.90	0.97	0.78	0.06	0.18
8 ACH	0.48 [0.32, 0.69]	0.71	0.92	*0.57*	0.06	0.05
		0.57	0.92	*0.72*	0.06	0.19
		0.89	0.90	*0.42*	0.16	0.13

ventilation of 4 ACH per Table 7-1 in ASHRAE 170-2021 *Ventilation of Healthcare Facilities* and the mass emission rates as determined in our study, and assuming a near-field as a 1 m^3 cube extending from the wiping surface to the worker with a local airspeed of 0.06 m/s, the near-field breathing zone exposure to a worker disinfecting with PAA in a similar wiping scenario would be almost twice the far-field exposure (Supplemental Fig. S3).

These results suggest that the use of PAA as a disinfectant by wiping in healthcare settings such as patient rooms or exam rooms, with general ventilation rates of 8 ACH or less, could pose a high risk of exposure to workers. Following the suggestions of the AIHA framework for an ECC 4 exposure, exposure reduction measures following the hierarchy of controls should be implemented in these settings. These measures include but are not limited to elimination and substitution of PAA where feasible, restricting use to areas with higher ventilation rates such as operating rooms that are often designed to 20 ACH, and the use of appropriate respiratory protection against PAA if other measures cannot maintain exposure levels below the STEL.

This study has several limitations that may affect the broad application of the results. First, previous research has shown that evaporation rates are chemical specific, with other methods proposed for estimating the evaporation rate for organic chemicals (Keil and Nicas 2003; Keil and Miller 2020) and aqueous acetic acid-based cleaners (Arnold et al. 2020). Previous results of other chemicals from the studies referenced above have indicated that conditions such as wind speed, temperature, humidity, thickness, and surface area of the pool of spilled material may affect the evaporation rate *K*. The results from this study indicate that the evaporation rate *K* for PAA was not significantly affected by the environmental conditions tested such as wind speed, which may be a result of the relatively high evaporation rate observed. However, the evaporation rate *K* was tested over a relatively short period, with an application of a limited mass, thickness, and surface area associated with a wiping task, and significant differences in these parameters may prove to affect the evaporation rate. As such, the model used to estimate the time-varying emission rate may only be useful for a relatively short duration wiping task where a thin layer of chemical is applied.

Additionally, the mass of PAA applied by each wipe in both the evaporation rate estimation and evaluation trials was difficult to control and varied significantly in successive trials and across various estimation methods. However, the use of probabilistic modeling in the evaluation trials accounted for this uncertainty in the applied mass. In future applications of this modeling method, the mass should be estimated specific to the task as it will vary relative to the disinfection procedures and worker.

The use of the WMR model to estimate concentrations is also a limitation, because in real-world occupational settings the local airflow is not often conducive to the perfect and immediate mixing assumed in the model. To account for imperfect mixing, simultaneous measurements from multiple locations within a room would better characterize far-field PAA concentrations, but only one direct-reading instrument was available to the authors. The modeling method used relied on a relatively short timestep (0.1 min) and there is a potential for autocorrelation in the successive readings from the PAA sensor at short timesteps that was not accounted for in the model. Also, if this model is used to aid in risk assessment purposes, there is an assumption that the estimated airborne concentrations would be representative of personal exposure concentrations for a worker exposed in this type of scenario.

Conclusion

We applied a time-varying mass emission rate, based on the small spill model, to estimate the concentration of PAA in conditions chosen to simulate those found during the task of wipe cleaning in typical healthcare settings. The results suggest that there is a high potential for overexposure when using PAA in healthcare settings, and that engineering and administrative controls must be considered when used in these settings. The PAA evaporation rate constant K can be applied to other scenarios involving surface cleaning using PAA. This technique is portable to a variety of similar surface cleaning scenarios and can be useful in screening-level assessments involving chemical mixtures. Additional work to determine the evaporation rate constant for a variety of chemicals could prove a valuable contribution to the methods available to occupational hygienists when conducting exposure assessments.

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Conflict of interest statement

The authors have no conflict of interest.

Data availability

The data underlying this article will be shared on reasonable request.

Supplementary material

Supplementary material is available at *Annals of Work Exposures and Health* online.

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